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RESOLUTION OF TRILINEAR MIXTURES: APPLICATION IN SPECTROSCOPY

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Abstract: Recent methodological development in three-way array analysis allows unique resolution of multicomponent linear mixtures in the absence of noise. When noise is present, an iterative linearization procedure based on a least squares formulation was proposed by Appellof and Davidson, but it requires good initial guesses which may be difficult to find in practical situations. In the paper, we describe an alternative procedure based on eigenanalysis, and we discuss the relationship between the two procedures. Even though the alternative procedure does not aim to minimize the squared residuals, it is, however, non-iterative and may be used to find initial values for the least squares procedure. An example using phase-resolved fluorescence spectroscopy data seems to indicate that only minor improvement may be expected from using the least squares procedure, and, for practical purposes, the estimates from the eigenanalysis procedure may be close enough to dispense with the least squares procedure.

Key words and phrases: Nonlinear least squares, eigenanalysis, resolution of trilinear mixtures, phase-resolved, fluorescence spectrometry, alternating least squares.

1. Introduction

In analytical chemistry and other related areas, a mixture can often be represented by a linear combination of rank one multidimensional arrays that are characteristic of the individual components in the mixture. For example, in fluorescence spectroscopy or gas chromatography/mass spectrometry, the representation occurs as a matrix, i.e. a two-way array. To resolve the mixture and identify the constituents, it is necessary to determine the individual arrays from that of the mixture. Over the years much attention has been paid to these two-dimensional data representations of mixtures and the associated bilinear model. However, the two-way analysis is limited because constituents which overlap in spectra cannot be uniquely resolved from a two-way mixture array (Warner (1982), Warner, et al. (1985), Borgen and Kowalski (1985), Burdick and Tu (1989)).

The inherent nonuniqueness of the two-way array approach has stimulated recent interest in the analysis of three-way array data. In contrast to two-way

arrays, noise-free three-way arrays can be uniquely resolved into their rank one constituents. However, there is a price to be paid when noise is present; the noise handling methods for three-way arrays are more complicated than for two-way arrays.

A natural approach is to estimate the constituent spectra of a three-way array by least squares, but minimization of the squared residual objective function is complicated by non-linearity and non-parametric forms of the constituent spectra. Appellof and Davidson (1981) developed an algorithm based on a linearization procedure which sets partial derivatives equal to zeros and linearizes the resulting equations by substituting the current best estimate of the solution. This iterative procedure, however, requires good initial values for each of the constituent spectra and considerable amount of computation because of the size of the data matrices involved. Furthermore, as noted by Appellof and Davidson, the procedure may perform poorly if the initial estimates are not close to the final least squares solution.

An alternative approach based on some intrinsic algebraic properties of the three-way arrays and the alternating least squares procedure has been recently proposed by Burdick et al. (1990) and, independently, by Sanchez and Kowalski (1990). This alternative procedure requires no initial guess and is non-iterative even though a few iterations are needed in the case of noise to reduce the amount of noise in the data matrices. The procedure, on the other hand, may not minimize the squared residuals. It is, therefore, interesting to see, whether for practical purposes, the estimates are close enough to the least squares solution and, if not, how much gain can be expected by using the least squares procedure.

In the paper, we first describe the formulation of the three-way model and the scientific background of phase-resolved fluorescence spectroscopy, which provides real-life examples of data arrays for the model. In Sections 3 and 4, we describe the linearization and eigenanalysis procedures and, finally in Section 5, we discuss the relationship between the two estimation procedures using a real sample mixture from the phase-resolved fluorescence spectroscopy.

2. The Three-Way Array Model

A general N-way array A is an array of real numbers which is subscripted by N indices i_n, i.e.,

$$A = (a_{i_1,\ldots,i_N}),$$

where $i_n \leq I_n$ and I_n are some positive integers for $1 \leq n \leq N$. The vector space of all such arrays will be denoted by $R^{I_1 \times \cdots \times I_N}$. A norm $\|\cdot\|$ can be defined on $R^{I_1 \times \cdots \times I_N}$ as

$$\|A\| = \left(\sum_{i_1, \ldots, i_N} a^2_{i_1, \ldots, i_N} \right)^{\frac{1}{2}} \tag{1}$$

for any $A = (a_{i_1, \cdots, i_N}) \in R^{I_1 \times \cdots \times I_N}$.

Let a_n be vectors in R^{I_n} for $1 \leq n \leq N$. The *tensor product* of these vectors, which we denote by

$$a_1 \otimes \cdots \otimes a_N,$$

is an N-way array $A = (a_{i_1, \ldots, i_N})$ for which

$$a_{i_1, \ldots, i_N} = a_{i_1} \cdots a_{i_N}.$$

An N-way array A is of *rank one* if there exist vectors a_n $(1 \leq n \leq N)$ for which

$$A = a_1 \otimes \cdots \otimes a_N .$$

The one-way, two-way and three-way array models are often used in fluorescence spectroscopy to display and represent the intrinsic spectral properties of a fluorescent species, which in turn also uniquely characterizes the species. For example, shown in Figures 3/(a) and (c) are the excitation and emission spectra of a fluorescent species as a function of wavelength. Here, the excitation spectrum characterizes the way the species absorbs the energy of light at different wavelengths and the emission spectrum displays the relative amount of energy released by the species afterwards at various wavelengths. Because these spectra are unique to each fluorescent species, they are often used as a "fingerprint" in identifying different species in a sample mixture. Even though the one-way array model for the excitation or emission spectrum is useful for characterizing a single component or one-species mixture, the two-way array model

$$M = \sum_{r=1}^{R} x_r \otimes y_r$$

where x_r and y_r denote the respective excitation and emission spectra for the rth component, is more useful for extracting constituent spectra from a multiple-component sample mixture (Warner (1982), Warner et al. (1985), Borgen and Kowalski (1985)). The observed data matrix for this model, which now is a function of both excitation and emission wavelengths, is referred to as the Excitation-Emission Matrix (EEM). However, as indicated in Section 1, this two-way array model still does not permit a unique resolution for the constituent spectra when there is overlap in spectra among constituents. Recent focus has been shifted

to the three-way array model which has been shown to have a unique decomposition of rank-one arrays. This result is quite remarkable, considering the non-parametric form of the spectra and the arbitrary number of components in the model (Burdick et al. (1990), Sanchez and Kowalski (1990)).

The three-way array model was recently used to fit the Excitation-Emission-Frequency Array (EEFA) which was built upon the EEM by adding another independent dimension: the fluorescence lifetime, which is the time required for fluorescence emission intensity to be reduced to $1/e$ of its initial intensity (McGown and Bright (1987)). The fluorescence lifetime, like the excitation and emission spectra, is another intrinsic property of a fluorescent species and when implemented through the phase modulation technique, which exploits the lifetime differences through the use of modulation frequency (McGown and Bright (1987), McGown and Millican (1988)), the measured relative emission intensity becomes a function of excitation, emission wavelengths and the modulation frequency. So if the relative intensity is recorded in a discretized range of excitation, emission wavelengths and modulation frequencies, the data can be expressed as a three-way model (assuming no interaction among the excitation, emission and modulation frequency):

$$S = \sum_{r=1}^{R} x_r \otimes y_r \otimes z_r \tag{2}$$

where $x_r \in R^I$, $y_r \in R^J$ and $z_r \in R^K$ are the excitation, emission spectra and modulation frequency vectors.

In fluorescence spectroscopy as well as in many other areas of analytical chemistry, interests often lie in resolving a multiple-component sample mixture. Of course, given an unknown mixture, it is first necessary to determine the number of components, R, in model (2). Even though this is by no means trivial and, as a matter of fact, is still a research topic under intensive investigations (Rossi and Warner (1986), Malinowski (1990), Tu et al. (1989), Wold (1978)), we will confine ourselves to the resolution problem below, assuming that we know the number R. So, given the observed data array S and R, to resolve the mixture we need to find the vectors x_r, y_r and z_r to satisfy Equation (2). In practical situations, the model always requires the addition of a noise term to reflect the random noise (either due to the instrument or the random behavior of molecules) contained in the data, which leads to the following model:

$$A = \sum_{r=1}^{R} x_r \otimes y_r \otimes z_r + N \tag{3}$$

where $S = \sum_{r=1}^{R} x_r \otimes y_r \otimes z_r$ is the signal array from the ideal model (2) and $N \in R^{I \times J \times K}$ is the noise term. To facilitate the discussion, we will refer to the

three dimensions of the array, namely, I, J and K, as "rows", denoted by $A^{(1)}$, "columns", denoted by $A^{(2)}$, and "layers", denoted by $A^{(3)}$, respectively. Using this definition, the ith row of A, for example, is the $J \otimes K$ matrix obtained by fixing the first index at i, i.e.

$$(A_i^{(1)})_{jk} = a_{ijk}. \tag{4}$$

Because of the noise term the measured array A will typically not be expressible in the form (2). The objective of the resolution analysis is to estimate the constituent vectors x_r , y_r and z_r (or the signal array S) from A. Adopting least squares (LS) as the estimation criterion, we seek the three-way array

$$\hat{S}^{(LS)} = \sum_{r=1}^{R} \hat{x}_r^{(LS)} \otimes \hat{y}_r^{(LS)} \otimes \hat{z}_r^{(LS)}$$

which minimizes the residual errors

$$\|A - \hat{S}^{(LS)}\|^2 = \min \|A - T\|^2 \tag{5}$$

over all three-way arrays $T = \sum_{r=1}^{R} \xi_r \otimes \eta_r \otimes \zeta_r$, where the norm $\|\cdot\|$ is as defined in (1).

3. The Appellof-Davidson Linearization Procedure

The Appellof-Davidson linearization procedure tries to minimize (5) by setting to zero its partial derivatives with respect to the components of x_r, y_r and z_r and attempting to solve the resulting equations. This approach leads to the following three sets of equations

$$\begin{aligned}
\sum_{r}^{R} x_{i,r} \left[\left(\sum_{j}^{J} y_{j,r}\, y_{j,r'} \right) \left(\sum_{k}^{K} z_{k,r}\, z_{k,r'} \right) \right] &= \sum_{j,k}^{J,K} A_{i,j,k}\, y_{j,r}\, z_{k,r'} \\
\sum_{r}^{R} y_{i,r} \left[\left(\sum_{i}^{I} y_{i,r}\, y_{i,r'} \right) \left(\sum_{k}^{K} z_{k,r}\, z_{k,r'} \right) \right] &= \sum_{i,k}^{I,K} A_{i,j,k}\, x_{i,r}\, z_{k,r'} \\
\sum_{r}^{R} z_{k,r} \left[\left(\sum_{i}^{I} x_{i,r}\, x_{i,r'} \right) \left(\sum_{j}^{J} y_{j,r}\, y_{j,r'} \right) \right] &= \sum_{i,j}^{I,J} A_{i,j,k}\, x_{i,r}\, y_{j,r'}.
\end{aligned}$$

The nonlinearity and high dimensionality of these equations make them difficult to solve directly, but if initial values are available for y_r and z_r, then the first set of equations can be solved for x_r. Similarly, the second and third sets of equations can be solved for y_r and z_r, respectively, given initial values for the other vectors. By repeating this process with the current values in place of the initial values for

the vectors x_r, y_r and z_r we obtain an iterative scheme for finding a solution, which can be put in the following matrix form

$$\begin{aligned} X^{(i+1)} &= Q(Y^{(i)}, Z^{(i)}, A)(P(Y^{(i)}, Z^{(i)}))^{-1} \\ Y^{(i+1)} &= Q(X^{(i)}, Z^{(i)}, A)(P(X^{(i)}, Z^{(i)}))^{-1} \\ Z^{(i+1)} &= Q(X^{(i)}, Y^{(i)}, A)(P(X^{(i)}, Y^{(i)}))^{-1}. \end{aligned} \tag{6}$$

Here

$$\begin{aligned} P(Y,Z) &= (Y'Y) * (Z'Z) \\ P(X,Z) &= (X'X) * (Z'Z) \\ P(X,Y) &= (X'X) * (Y'Y), \end{aligned}$$

where $X = (x_1, \ldots, x_R)$, $Y = (y_1, \ldots, y_R)$ and $Z = (z_1, \ldots, z_R)$ and $*$ denotes elementwise multiplication. $Q(Y, Z, A)$ is a $I \times R$ matrix with its ith row given by the diagonal elements of $Y'A_i^{(1)}Z$, $Q(X, Z, A)$ is a $J \times R$ matrix with its jth row given by the diagonal elements of $X'A_j^{(2)}Z$ and $Q(X, Y, A)$ is a $K \times R$ matrix with its kth row given by the diagonal elements of $X'A_k^{(3)}Y$, where $A_m^{(n)}$ is defined as in (4).

The above iterative scheme was proposed by Appellof and Davidson (1981). They observed that the procedure converges slowly and may not converge to the global minimum of (5) unless the initial values are made close to the final solution. It may be difficult in practice to obtain such starting values. How to find good starting values to guarantee convergence and to speed up convergence can be a difficult problem. A possible solution is given by the eigenanalysis procedure described in the next section. It yields estimates which can be used as the initial values for the iterative Appellof-Davidson procedure. In fact, estimates from the eigenanalysis procedure may be so close to the least squares estimates that we can dispense with the Appellof-Davidson procedure altogether. An illustrative example with real data is presented in Section 5.

4. The Eigenanalysis Procedure

An alternative approach is the eigenanalysis procedure proposed by Burdick et al. (1990) and by Sanchez and Kowalski (1990). It eliminates the need for initial values by utilizing the tensor structure of three-way arrays. An important property of a three-way array of rank R is its ability to be resolved uniquely into its rank one constituents, provided that R is not too large. Resolution of a rank R array into its constituents is a major part of the eigenanalysis procedure. The other part is essentially a noise reduction procedure. It is accomplished by fitting

a rank R array to a measured array of higher rank containing signal plus noise. We begin this section by describing the resolution methodology in the absence of noise and continue by describing the methodology for finding a rank R fit to a measured array.

The crux of the eigenanalysis procedure is the unique decomposition of the signal array S in (2). Let $X = (x_1, \ldots, x_R)$, $Y = (y_1, \ldots, y_R)$ and $Z = (z_1, \ldots, z_R)$. Let $S_k^{(3)}$ be the kth layer of S. Then it can be easily established from (2) that

$$S_k^{(3)} = X \operatorname{diag}(z_{k,\rightarrow}) Y' \tag{7}$$

where $z_{k,r}$ denotes the element of Z on its kth row and rth column and $\operatorname{diag}(z_{k,\rightarrow})$ is an $R \times R$ diagonal matrix with $z_{k,r}$ in the rth diagonal position. It follows that the layers of S have the same column space $\operatorname{Col}(X)$ and row space $\operatorname{Col}(Y)$.

Now let $U = (u_1, \ldots, u_R)$ and $V = (v_1, \ldots, v_R)$, where u_i and v_i are orthonormal bases for $\operatorname{Col}(X)$ and $\operatorname{Col}(Y)$, respectively. It therefore follows from (7) that there exist matrices P and Q such that

$$\begin{aligned} X &= UP \\ Y &= VQ \\ \operatorname{diag}(z_{k,\rightarrow}) &= P^{-1} L_k (Q')^{-1}, \end{aligned} \tag{8}$$

where $L_k = U' S_k^{(3)} V$. A little algebra shows that P and Q can be determined by

$$\begin{aligned} \operatorname{diag}(z_{i,\rightarrow})(\operatorname{diag}(z_{j,\rightarrow}))^{-1} &= P^{-1} L_i L_j^{-1} P \\ &= Q^{-1} L_i' (L_j')^{-1} Q, \end{aligned} \tag{9}$$

for any $i \neq j$. Note that the columns of P and Q are eigenvectors of $L_i L_j^{-1}$ and $L_i'(L_j')^{-1}$ respectively. So, if $L_i L_j^{-1}$ has distinct eigenvalues for some i and j then such P and Q are unique.

This eigenanalysis procedure can be applied to any appropriate pair of layers from an array which has the form (2). Unfortunately, it cannot be applied directly to the measured array A. The presence of noise in A will generally cause its rank to exceed R, the number of components in the mixture. Before the eigenanalysis just described can be applied, we must extract an estimated rank R signal from the measured array containing signal plus noise.

There are two steps to the signal extraction process. As a consequence of (2), the layers of S are $I \times J$ matrices which have a common R-dimensional column space, spanned by the x_r, and a common R-dimensional row space, spanned by the y_r. The measured array will not have this property because of noise. The first step, therefore, is to replace the measured array A by a fitted array $\hat{A}$ whose

layers have a common R-dimensional row space and a common R-dimensional column space. Using least squares as the criterion of fit yields

$$\|A - \hat{A}\|^2 = \min \|A - B\|^2 \tag{10}$$

over arrays B whose layers have a common R-dimensional column space and a common R-dimensional row space. It can be shown that such an array $\hat{A}$ always exists (Tu (1989)).

The fitted array $\hat{A}$ may or may not have rank R. If not, then as a second step we must find an estimated signal $\hat{S}$ of rank R which fits $\hat{A}$ as closely as possible.

The first step is accomplished by the method of alternating least squares (ALS) (Kroonenberg and de Leeuw (1980)). Let U be an $I \times R$ matrix whose columns span the common column space and V be an $J \times R$ matrix whose columns span the common row space. The ALS minimizes (10) by alternating between the two conditional maximizations

$$\text{trace}\left\{P_V \left[\sum_{k=1}^{K} \left(A_k^{(3)}\right)^T P_U A_k^{(3)}\right] P_V\right\} \tag{11}$$

given U and

$$\text{trace}\left\{P_U \left[\sum_{k=1}^{K} A_k^{(3)} P_V \left(A_k^{(3)}\right)^T\right] P_U\right\} \tag{12}$$

given V, where $P_U = U(U^TU)^{-1}U^T$ denotes the projection matrix. The maximums in (11) and (12) occur when the columns of V and U are the eigenvectors of

$$\sum_{k=1}^{K} \left[A_k^{(3)}\right]^T P_U A_k^{(3)}$$

and

$$\sum_{k=1}^{K} A_k^{(3)} P_V \left[A_k^{(3)}\right]^T$$

corresponding to their R leading eigenvalues, respectively. The procedure is initiated by using either the eigenvectors of

$$\sum_{k=1}^{K} A_k^{(3)} \left[A_k^{(3)}\right]^T$$

as the starting value for U, or, alternatively, those of

$$\sum_{k=1}^{K} \left[A_k^{(3)}\right]^T A_k^{(3)}$$

as that for V. This iterative procedure is guaranteed to converge (Tu (1989)). Our experience seems to show that only a few iterations, usually three or four, are needed for the procedure to converge.

After $\hat{A}$ has been obtained, we can find matrices $\hat{U}_{I\times R}$ and $\hat{V}_{J\times R}$ whose columns are arbitrarily chosen orthonormal bases for the respective common column and row spaces of the layers $\hat{A}_k^{(3)}$. From $\hat{U}$ and $\hat{V}$ we get $\hat{L}_k$ by

$$\hat{L}_k = \hat{U}' A_k^{(3)} \hat{V}.$$

At this point we can apply eigenanalysis to the $\hat{L}_k$ as in (9) to find $\hat{P}$ and $\hat{Q}$. However, in contrast to the noise-free case, it now may make a difference which pair $(\hat{L}_i, \hat{L}_j)$ is selected for the eigenanalysis. If $K = 2$, there is only one pair available, but if $K \geq 3$, there are multiple possible pairs that could be used in the analysis. Using a pair of linear combinations of the $\hat{L}_k$ is also an option. Sanchez and Kowalski (1990) have recommended using a pair of linear combinations derived from a singular value decomposition of the $\hat{L}$ array.

The Sanchez-Kowalski procedure can be described briefly as follows. Let B denote the $K \times R^2$ matrix whose kth row is obtained by unfolding the $R \times R$ matrix $\hat{L}_k$ into a $1 \times R^2$ row vector. Let b_1 and b_2 denote the eigenvectors of BB' corresponding to the two largest eigenvalues. Let $\hat{L}_1^*$ and $\hat{L}_2^*$ be the $R \times R$ matrices obtained by refolding $b_1'B$ and $b_2'B$, respectively. Obtain $\hat{P}$ and $\hat{Q}$ by applying eigenanalysis to $\hat{L}_1^*$ and $\hat{L}_2^*$, as in (9). Then substitute $\hat{P}$ and $\hat{Q}$ into (8) to get $\hat{X}$, $\hat{Y}$ and $\hat{Z}$.

5. Results and Discussion

In this section, we compare the LS estimates and the estimates obtained from the eigenanalysis procedure using a real sample mixture, which consists of two fluorescent components: 9, 10 diphenylanthracene (DPA) and anthracene (ANT). The observed three-way EEFA is a $30 \times 30 \times 5$ array with 30 excitation wavelengths from 330 to 448 nm, 30 emission wavelengths from 380 to 498 nm and 5 modulation frequencies at 5, 10, 20, 40, 80 MHz. For comparison purposes, the EEFA's for each of the individual components are also obtained in the same format. Shown in Figure 1 are four of the layers of the mixture corresponding to frequencies at 5, 10, 40 and 80 MHz. Plotted in Figure 2 are the layers of ANT and DPA at 10 MHz. Strong spectral overlap between the two components is easily seen from these plots.

Using the three-way model in (3), the vectors x_r and y_r represent the excitation spectrum and emission spectrum for the rth component, and the vector z_r represents the phase-resolved emission intensities for the rth component corresponding to the different modulation frequencies. Theoretically, the elements

of the Z matrix should be described by

$$z_{k,r} = c_r \frac{\omega_k \tau_r}{1 + \omega_k^2 \tau_r^2}$$

where τ_r denotes the fluorescence lifetime for the rth component, ω_k denotes the kth modulation frequency, and c_r depends mainly on the concentration of the component (Burdick et al. (1990)). It can be easily verified that if $\tau_r \neq \tau_{r'}$ and $\omega_k \neq \omega_{k'}$

$$\text{diag}(z_{i,\rightarrow})(\text{diag}(z_{j,\rightarrow}))^{-1}$$

will have distinct elements on the diagonal. So the matrices P and Q can be uniquely determined at least in the absence of noise. In practice, if the noise level is relatively low, this property will still be preserved (Tu (1989)).

The resolved vectors from the eigenanalysis procedure are plotted in Figure 3. Note that the overall agreement between the resolved and standard (resolved from the single compound EEFAs) is very good but slightly better for DPA than for ANT.

The LS estimates were obtained from the iterative linearization procedure in (6) using vectors resolved from the eigenanalysis procedure as starting values. The iteration was continued beyond the $(i+1)$st step unless the maximum of the average squared residuals of

$$\|X^{(i+1)} - X^{(i)}\|^2/60$$

$$\|Y^{(i+1)} - Y^{(i)}\|^2/60$$

$$\|Z^{(i+1)} - Z^{(i)}\|^2/10$$

fell below 0.5×10^{-6}. By this criterion the procedure converged at step 15. So $x_r^{(15)}$, $y_r^{(15)}$ and $z_r^{(15)}$ were taken to be the LS estimates.

The sum of squared residual errors

$$\left\| A - \sum_{r=1}^{2} x_r^{(i)} \otimes y_r^{(i)} \otimes z_r^{(i)} \right\|^2$$

was also checked at each iteration. Table 1 lists these values for some of the iteration steps.

It is of interest to compare the starting values obtained from the eigenanalysis procedure with the end result of the iterative linearization procedure. This comparison can be made in at least two ways. First we can look at the sum of squared residuals

$$\|A - \hat{S}\|^2.$$

This value for the eigenanalysis procedure ($\hat{S} = \hat{S}^{(EA)}$) is 0.706641, which compares to the least squares value 0.706377 ($\hat{S} = \hat{S}^{(LS)}$). As expected, these values are very close, which is important to ensure convergence of the linearization procedure.

In addition, we can calculate a bound for the amount of improvement in the criterion that can be achieved by the iterative linearization procedure. If $\hat{A}$ is defined as in (10), it follows that

$$\|A - \hat{A}\|^2 \leq \|A - \hat{S}^{(LS)}\|^2 \leq \|A - \hat{S}^{(EA)}\|^2.$$

In our example these values are:

$$\begin{aligned} \|A - \hat{A}\|^2 &= 0.700349 \\ \|A - \hat{S}^{(LS)}\|^2 &= 0.706377 \\ \|A - \hat{S}^{(EA)}\|^2 &= 0.706641. \end{aligned}$$

Since $\hat{A}$ is obtained in the first step of the eigenanalysis procedure, we know before starting the linearization procedure that the maximum reduction in the criterion that it can achieve is 0.006292. We thus have the option of aborting the iterative linearization process if we decide that the maximum possible improvement is not worth the extra effort.

Second, we can compare the differences between the eigenanalysis and least squares estimates of the spectral vectors. Plotted in Figures 3 and 4 are these estimated vectors, together with the standard vectors, which are obtained from the single compounds. Visual inspection shows that the eigenanalysis procedure gives good estimates that are indistinguishable from the least squares estimates. Note that there is still some discrepancy between the LS estimated and the standard excitation vectors. The same estimated excitation vector was obtained at convergence of the LS procedure (with the same convergence criterion as before), even with the standard vectors as starting values. So, it seems that this discrepancy is attributed to the noise in the mixture EEFA, not to the starting values.

To compare these estimated vectors quantitatively, we used the Uncorrected Array Correlation (UAC), which is defined as

$$\mathrm{UAC}(A, B) = \frac{\sum_{i_1,\ldots,i_N} a_{i_1 \cdots i_N} b_{i_1 \cdots i_N}}{\|A\| \, \|B\|}$$

for any N-way arrays $A = (a_{i_1 \cdots i_N})$ and $B = (b_{i_1 \cdots i_N}) \in R^{I_1 \times \cdots \times I_N}$. The UAC is a generalization of the uncorrected correlation between vectors.

An interesting and useful result about UACs of rank one arrays is given by the following theorem.

Theorem 1. *If A and B are two rank one arrays, i.e.*

$$\begin{aligned} A &= a_1 \otimes \cdots \otimes a_N \\ B &= b_1 \otimes \cdots \otimes b_N \end{aligned}$$

then

$$\mathrm{UAC}(A, B) = \prod_{n=1}^{N} \mathrm{UAC}(a_n, b_n).$$

Since the proof is straightforward, it is omitted.

The UAC's between the vectors obtained from the eigenanalysis alone and eigenanalysis plus linearization estimation procedures are listed in Table 2. Listed in Table 3 are the UAC's between the estimated vectors obtained from the single compounds (standard) and the mixture by both procedures. Also listed are the UACs for the entire EEFAs, which, by Theorem 1, can be calculated as the products of the UACs of the corresponding vectors of the arrays. These tables confirm that the eigenanalysis estimates are quite close to the least squares estimates.

In summary, the eigenanalysis, although it uses least squares as a method of noise reduction, does not produce the least squares fit of rank R to a given array. It is reasonable to expect, however, that the eigenanalysis estimate will be close to the least squares estimate and that it will therefore be useful, either as it stands or as a starting estimate for the Appellof-Davidson linearization procedure, which seemed to be confirmed by our example.

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Table 1. The squared residual errors $\|A - \sum_{r=1}^{2} x_r^{(i)} \otimes y_r^{(i)} \otimes z_r^{(i)}\|^2$ and the convergence criterion determined by the maximun of the average squared residuals between successive estimated vectors for some values of the iteration steps.

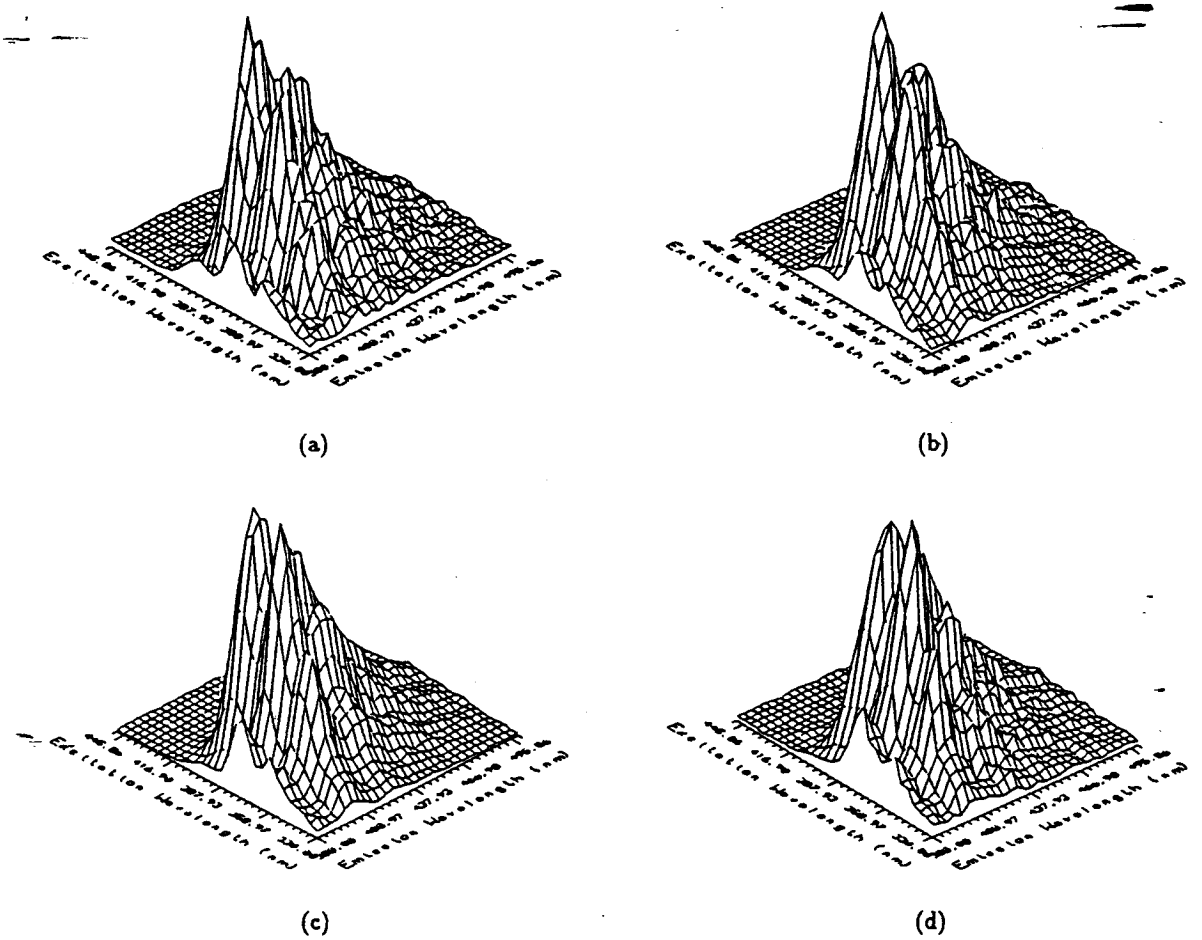
Iterations	1	2	3	10	15
Sqd res errors	0.7066407	0.7063781	0.7063771	0.7063770	0.7063769
Convergence criterion	0.7×10^{-4}	0.2×10^{-4}	0.7×10^{-6}	0.5×10^{-6}	0.3×10^{-6}

Table 2. The UAC's between the estimated vectors and EEFA's from the eigenanalysis (EA) and eigenanalysis plus linearization (LS) procedures.

	UAC			
Component	Excitation ($\hat{x}^{EA}$, $\hat{x}^{LS}$)	Emission ($\hat{y}^{EA}$, $\hat{y}^{LS}$)	Phased-resolved emission ($\hat{z}^{EA}$, $\hat{z}^{LS}$)	EEFA ($\hat{S}^{EA}$, $\hat{S}^{LS}$)
ANT	0.999992	0.999992	0.999996	0.99998
DPA	0.9999995	0.9999996	0.99999999	0.999999

Table 3. The UAC's between the estimated vectors and EEFA's obtained from the single compounds and the mixture by the two estimation procedures.

Component	Excitation	Emission	Phased-resolved emission	EEFA
	Eigenanalysis			
ANT	0.991754	0.998657	0.999889	0.99031
DPA	0.999929	0.999510	0.999919	0.99936
	Least squares			
ANT	0.991781	0.998664	0.999890	0.99034
DPA	0.999929	0.999516	0.999919	0.99936



Fiqure 1. Plots of the layers for the mixture of ANT and DPA (a) at 5 MHz (b) at 10 MHz (c) at 40 MHz (d) at 80 MHz.

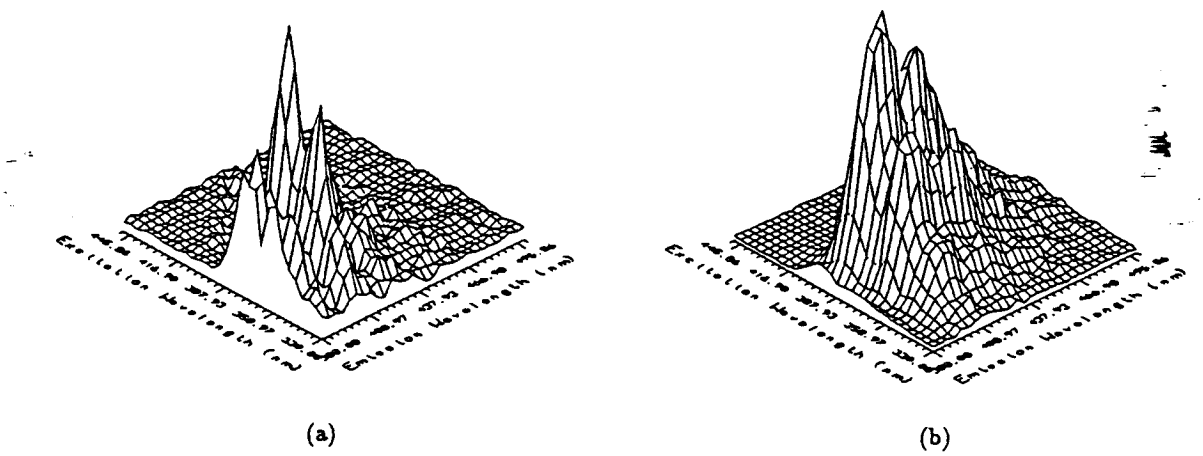


Figure 2. Plots of the layers at 10 MHz for the single compounds of (a) ANT and (b) DPA.

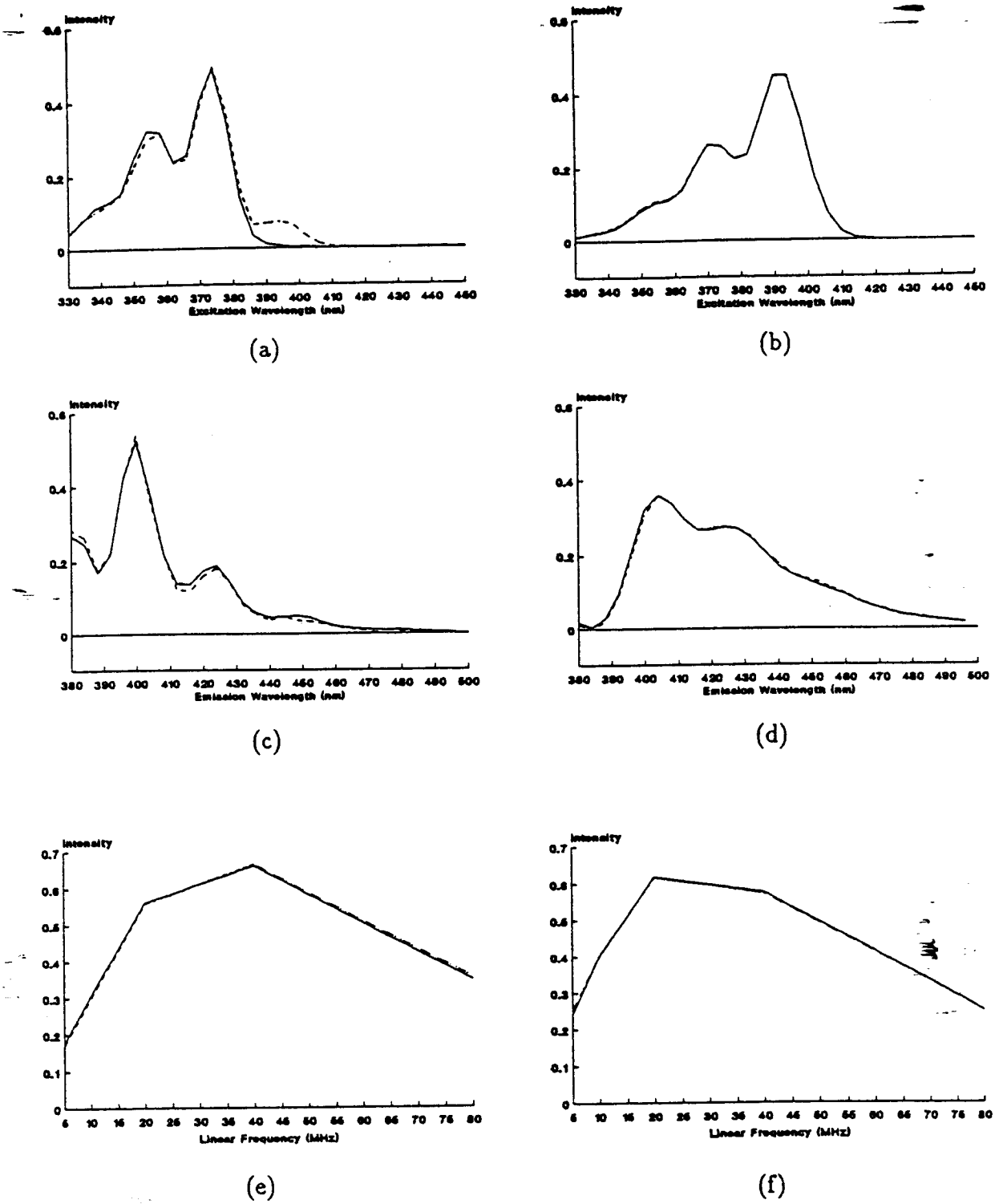


Figure 3. Plots of the standard vectors (solid line) and the estimated vectors from the eigenanalysis procedure (broken line). Excitation: (a) ANT (b) DPA; Emission: (c) ANT (d) DPA; Phase-resolved emission: (e) ANT (f) DPA.

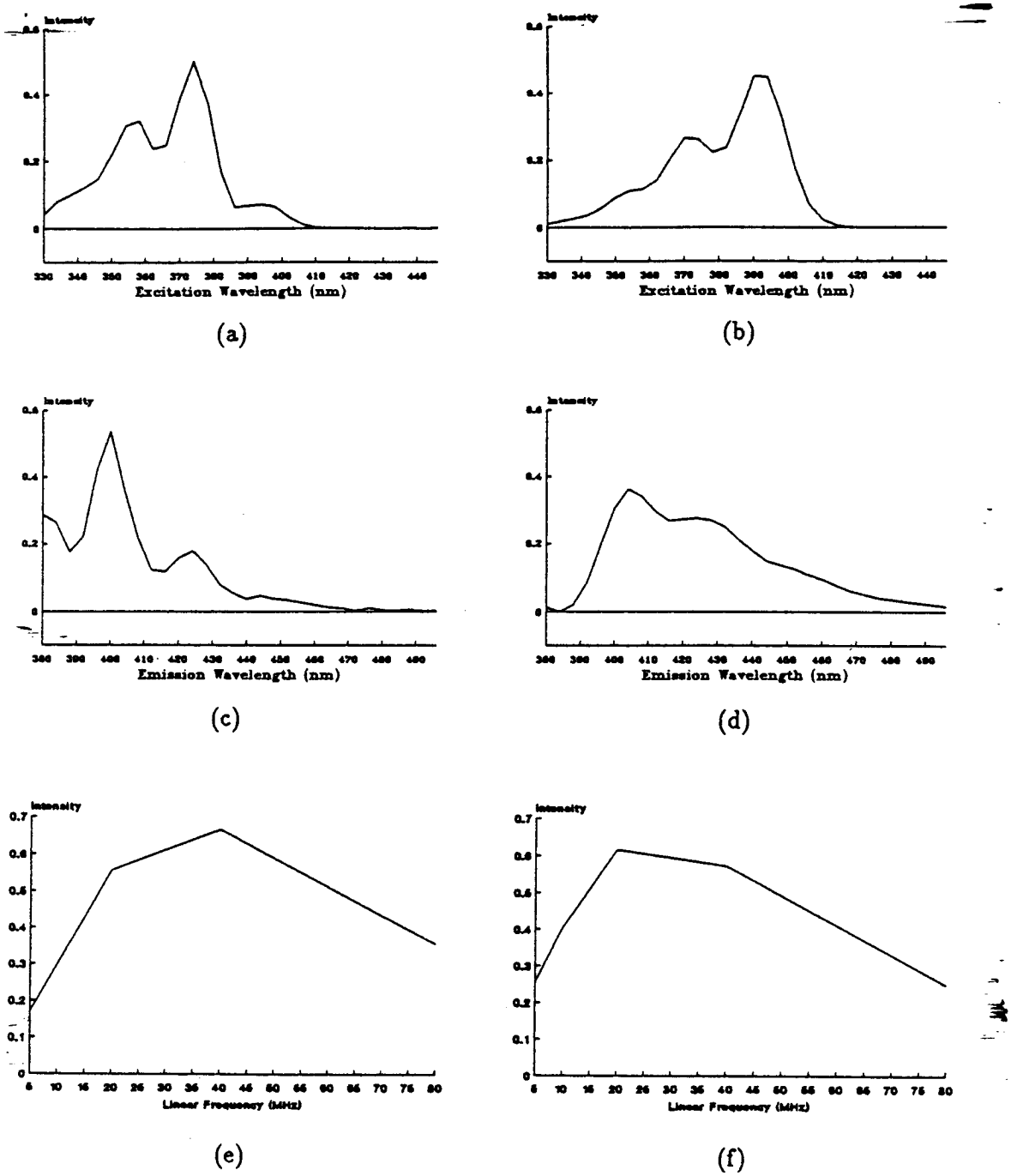


Figure 4. Plots of the LS estimates (solid line) and the estimates obtained from the eigenanalysis procedure (broken line). Excitation: (a) ANT (b) DPA; Emission: (c) ANT (d) DPA; Phased-resolved emission: (e) ANT (f) DPA.

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